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# Mesoporous Silica Impregnated by NI and Nimo as Catalysts for Hydrocracking of Waste Lubricant

**Nurmalasari, Wega Trisunaryanti*, Sutarno, Iip Izul Falah**

**Department of Chemistry, Faculty of mathematics and natural sciences**
**Universitas Gadjah Mada Sekip Utara Yogyakarta, Indonesia 55281**

**Abstract :** Impregnated of Ni and NiMo on mesoporous silica (SM) as catalysts in hydrocracking of waste lubricant has been evaluated. The SM was synthetized using gelatin of bovine bone as a template. Extraction of the gelatin was carried out using acid and alkaline solution followed by hydrolysis. The gelatin was analyzed by Fourier Transform Infra Red Spectrophotometer (FTIR and that of the SM was characterized by FTIR, Surface Area Analyzer (SAA) and Transmission Electron Microscopy (TEM). The nickel was loaded onto the SM (Ni/SM Catalyst) by wet impregnation while the NiMo$_{(s)}$/SM catalyst was prepared by co-impregnation and that of by sequential impregnation. The catalysts were characterized using Atomic Absorption Spectroscopy (AAS), Scanning Electron Microscope (SEM), SAA, and gravimetric method. Activity of catalysts was tested in hydrocracking of waste lubricant. The result showed that maximum gelatin yield, was 10.69 wt.% extracted at 90 ˚C and consisted of Amide A, B, I, II dan III. The SM had pore diameter, specific surface area and pore volume of 7.98 nm, 550 m$^2$/g and 1.10 cm$^3$/g, respectively and showed wormhole-like structure. Total acidity of SM, Ni/SM, NiMo$_{(s)}$/SM and NiMo$_{(c)}$/SM samples was 5.1; 7,1; 6.7 and 7.3 mmol/g. The highest liquid product was achieved by NiMo$_{(c)}$/SM catalyst (43.22 wt.%) with the selectivity for gasoline and diesel fractions was 9.42 and 33.82 wt.%.

**Keywords**: Gelatin, silica, mesopore, catalyst, hydrocracking, lubricant.

## Introduction

The Quality of lubricating oil of motor vehicles will decline during engine operation even can be contaminated by dangerous heteroatom. The numbers are increased that can cause seriously problem in our environment if not handled properly. To reduce the negative impact caused by the waste lubricant toward the environment, recycling process of the lubricant into fuel oil was the best method[1-3]. The process can be performed by hydrocracking[4-9]. The thermally and catalytically hydrocracking process of the waste can be taken to produce lighter hydrocarbon molecule that can be used as a fuel. Catalytically cracking process requires a catalyst with a corresponding characters towards the reactants. The catalyst commonly are transition metals[10-12]such as Ni, Mo, Co and Ni/Mo or Co/Mo. The catalyst preparation method influenced the activity and selectivity of catalyst[11-18]. The metal have to spread out into the surface of a porous material to increase its surface area and prevent it from sintering. The mesoporous support material is required for hydrocracking of high molecular weight feed. The mesoporous materials can be prepared using an appropriate template.

Some synthetic surfactants as a template in synthesis of mesoporous material is difficult to degraded and caused eutrophication in water and environmental pollution. Gelatin is a protein obtained by hydrolysis of collagen of bone component[19]orskinof mammals[20,21] can be used as a template in mesoporous material synthesis[22-24]. Gelatin derived from bovine bone is gelatin A, because it is extracted by using acid. In addition, the use of acid produces higher yields of gelatin. Temperature treatment and duration of the hydrolysis process greatly affect the shape of the gelatin molecules. Decomposition of the gelatin form a single helical structure that influent the formation of mesoporous silica[24].

Based on the above explanation, the authors carried out synthesis of mesopore silica (SM) using gelatin as template. Nickel metal was impregnated into the SM produced Ni/SM catalyst. Impregnation of NiMo onto the SM was carried out by sequential and co-impregnation method produced the $NiMo_{(s)}$/SM and $NiMo_{(c)}$/SM. The catalysts activities were tested in hydrocracking of waste lubricant to produce gasoline and diesel fractions. The comparison of these catalysts characters and activities were the main objective of the present work.

## Experimental

### Material

Bovine bone from various traditional market in Yogyakarta, hydrochloric acid analytical grade was purchased from Fluka (Japan), sodium hydroxide,glacial acetic acid, sodium silicate, and sulfuric acid analytical gradewere obtained from E. Merck (Germany), nickel nitrate hexahydrate, ammonium molybdate tetrahydrate, waste lubricant supplied by automotive market in Yogyakarta.

### Methods

The extraction of gelatin was carried out according to Ulfa et al.[19]. The gelatin was then characterized by FTIR (FTIR-8201 PC Shimadzu).

Gelatin and sodium silicate were dissolved in demineralized water at 40 ˚C. Sulfuric acid 0.1 M was added to sodium silicate solution to get acidified silicate stock at pH 4. Gelatin solution was then added to the acidified silicate stock and the mixture was stirred for 1 h. The gel solution was transferred into autoclave and hydrothermally treated at 100 ˚C for 24 h. Finally, the product was filtered, washed with aquadest, dried at 80 ˚C and calcined at 550 ˚C for 5 h (produced SM). The SM was then analyzed by FTIR, Surface Area Analyser (SAA) Quantachrome NovaWin versi 11.0 and TEM (JEOL JEM-1400).

The Ni/SM catalyst was prepared by dissolved the SM into nickel nitrate hexahidrate solution. The solution was refluxed at a temperature of 90°C for 4 h and then dried in oven at $100^oC$.Preparation of $NiMo_{(c)}$/SM catalyst was done by dissolving 1 g of the SM in the ammonium molibadate tertahidrate and nickel nitrate hexahidrate salt solution followed by refluxing the solution at a temperature of 90 °C for 4 h. After that, the solution was evaporated and dried in oven at $100^oC$. The $NiMo_{(s)}$/SM catalyst was prepared by dissolving 1 g of the SM sample in a ammonium molibadate tertahidrate solution. The solution was then refluxed at a temperature of 90 °C for 4 h followed by drying in oven at temperature of 90°C for 3 h. The dried sample was then dissolved in a nickel nitrate hexahidrate solution then refluxed at a temperature of 90°C for 4 h and dried in an oven at 90 °C for 3 h. All catalysts were calcined under $N_2$ gas at $450^oC$ for 2 h followed by oxidation with $O_2$ gas at $45^oC$ for 2 h and reduced with $H_2$ gas $450^oC$ for 2 h. Each treatment was carried out with a gas flow rate of 15 mL/min. The Ni/SM, $NiMo_{(s)}$/SM and $NiMo_{(c)}$/SM catalysts were characterized using FTIR, TEM, SEM and AAS.

Hydrocracking process was performed at atmospheric pressure, temperature of 450 $^oC$ and catalyst to feed weight ratio of 1:10. The catalyst and feed were introduced into the reactor and put into the heating furnace. Liquid products obtained from the hydrocracking were analyzed by GC-MS to determine the type of the compounds and liquid product conversion. The catalyst selectivity toward gasoline and diesel fraction was determined based on the results of GC-MS and weight of the liquid product.

## Results and Discussion

### Characterization of Bovine Bone Gelatin

The peak shape, wave numbers, and the whole intensity of the wave is used to characterize the differences in the structure of the material.

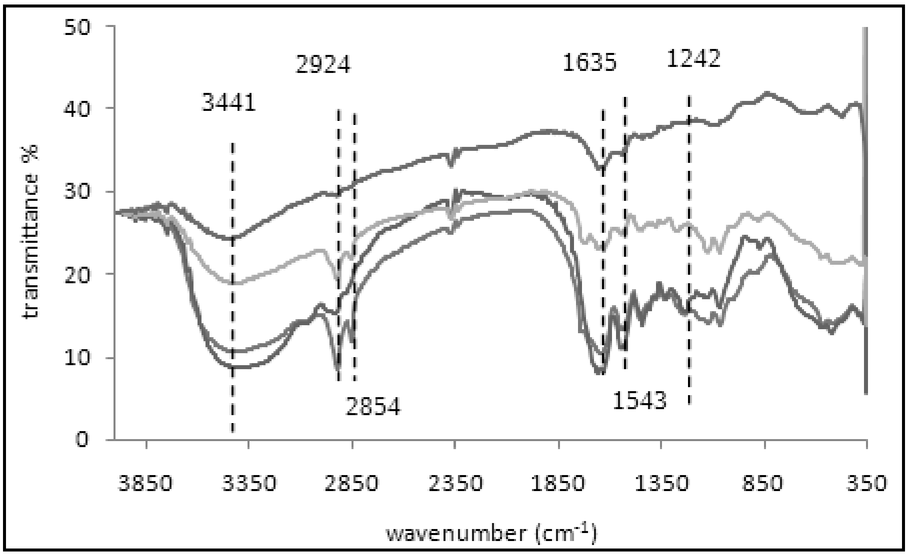


**Fig. 1 FTIR Spectra of Bovine bone gelatin: (a) Gelatin standard (power food Grade, PFG), gelatin hydrolysis at (b) 50°C, (c) 70°C and (d) 90°.**

Figure 1 showed the spectra of bovine bone gelatin extracted at different temperatures. According to Muyonga et al.[20]there are five absorptions of functional groups of gelatin. Amide A located at wave number of 3600-3400 cm$^{-1}$, was an absorption area of NH and OH stretch. The area of 3000-2800 cm$^{-1}$, was an absorption band of amide B shows the symmetry $CH_2$ vibration. Amide I areas is a stretch vibration of C = O (80%) were paired with NH bending vibrations (<20%). Amide II absorption area is 1575-1480 cm$^{-1}$ which is the NH bending vibrations and CN strains. The Absorption at 1240-670 cm$^{-1}$ showing a combination of C-N stretching vibration and deformation NH of the amide linkage and absorption arising from $CH_2$ wagging vibration was called the amide III. Based on the FTIR results in Figure 1, the bovine bone gelatin consists of Amide A, B, I, II dan III.

## Characterization of SM

### Characterization by FTIR

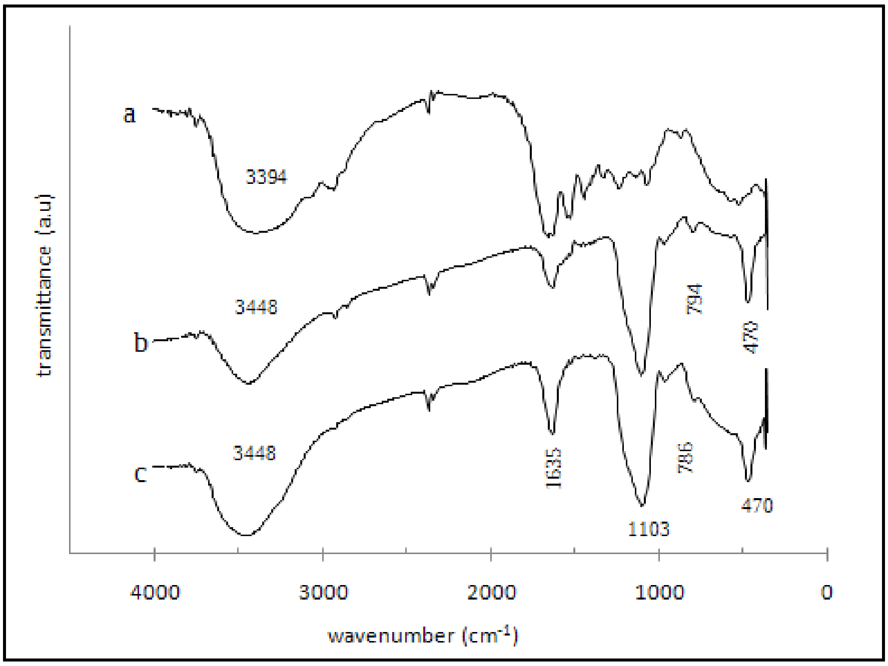


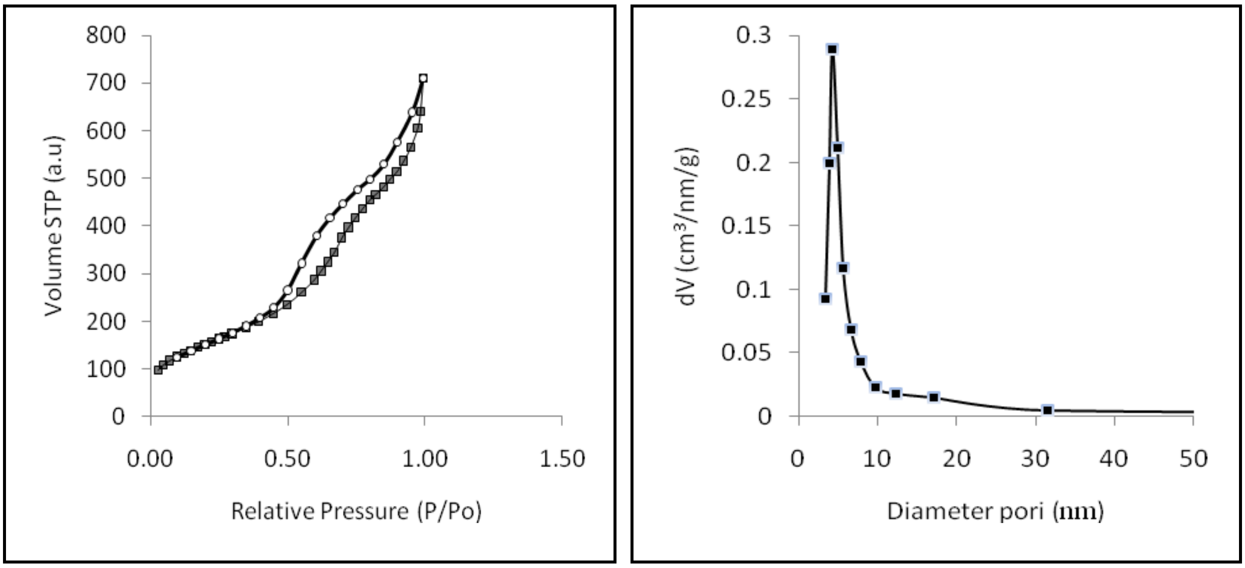
**Fig. 2 FTIR Spectra of (a) Gelatin; SM: (b) before and (c) after calcinations.**

The FTIR spectra in Figure 2(a) showed gelatin extracted at a temperature of 90°C.Absorption band which appears at wave number of 3394 $cm^{-1}$ was a vibration strain of NH paired with OH group. Symmetric and an asymmetric C-H was observed at wave number of 3078 $cm^{-1}$ and vibration of $CH_2$ functional groups was at 2931 $cm^{-1}$.The wave numbers of 1635 and 1527 $cm^{-1}$ was belonged to vibration of C=O and NH bending (primary amine)[7,10].

Figure 2(b) showed absorption silica functional groups of 1103, 1635, 972 and 470 $cm^{-1}$, while the functional groups of gelatin was of 2924, 2854 and 1543 cm-$^{1}$.The hydrothermal process cannot be used to eliminate all of gelatin. The content of gelatin after hydrothermal processes was 20 wt%, therefore, the calcinations was done to produce silica material without gelatin[15]. The absorption of 2924, 2854 and 1543 $cm^{-1}$ observed in Figure 2(b). This indicate that the calcinations are effective to remove gelatin from the mesoporous silica.

The strong absorption at wave number of 1103, 786, and 470 $cm^{-1}$ on the material synthesized showed in Figure 2(c). The wave number was associated with condensed silica. Peak at wave number 786, and 470 $cm^{-1}$ may be indicated as symmetrically strain and deformation of the Si-O-Si, while the absorption around 1103 $cm^{-1}$ was associated with a strain bridge vibration of Si-O-Si. The next peak in 3425 and 1627 $cm^{-1}$ indicated as a species of silanol (Si-OH). The FTIR interpretation results indicated that the SM was successfully synthesized using a bovine bone gelatin as a template. This result similar to the search conducted by Wang et al.[23] and Hsu et. al.[24]

**Characterization by SSA (*Surface Area Analyser*)**



**(a)** **(b)**

**Fig 3. (a) Isotherm Adsorption-desorption and (b) The pore diameter distribution of SM**

The results of adsorption-desorption curve by the SSA analysis in Figure 3(a) showed that the SM was a mesoporous material. It was consistent with those reported by Setyawan and Balgis[22], Wang et. al.[23] and Hsu et. al.[24]whose controlled the pore of the silica using synthetic gelatin as a template. Figure 3(b) showed that the SM had a narrow pore diameter distribution between 3.41 and 7.87 nm with dominant pore diameter distribution at 4.93 nm which included in category of mesoporous material[25-29].

Based on the SAA data the SM has an average pore diameter of 7.98 nm calculated by the Barrett-Joyner-Halenda (BJH) equation. Specific surface area of the SM calculated by the Brunaeur-Emmett-Teller (BET) method was 550.08 $m^2$/gram. These results indicated that the mesopore silica had been successfully synthesized using bovine bone gelatin as a template.

### Characterization by TEM (*Transmission Electron Microscopy*)

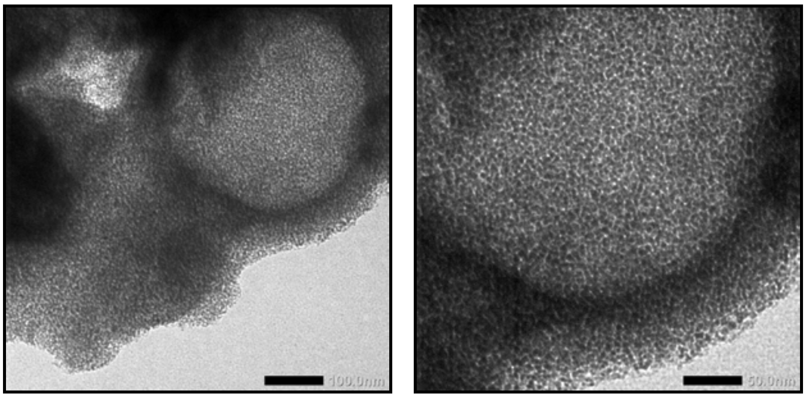


**Fig. 4 TEM image of synthesized mesoporous silica**

Figure 4 showed that the mesoporous silica has a wormhole-like pore structure. It was appropriate to that reported by Wang et al.[23] who produced mesoporous silica with a wormhole-like pore structure using gelatin as a template agent of mesopore structure.

### Characterization of the metal loaded-SM Catalysts

Characters of metal loaded-SM catalysts which included metal content and acidity were shown in Table 1.

**Table 1. Metal Content dan Catalyst Acidity of silica**

| Catalyst | Metal Content | | Total Acidity (mmol/g) |
|---|---|---|---|
| | Ni (wt.%) | Mo (wt.%) | |
| Silica (SM) | - | - | 5,1 |
| Ni/SM | 0,9 | - | 7,1 |
| NiMo$_{(s)}$/SM | 0,01 | 0,52 | 6,7 |
| NiMo$_{(c)}$/SM | 0,12 | 0,92 | 7,3 |

Table 1 showed that dispersion of Ni and Mo metals onto the SM increased its acidity. This results may be caused by the characteristics of Ni and Mo metals which have the Lewis acid sites. The NiMo$_{(c)}$/SM catalyst had the highest acidity compared to the others, while the NiMo$_{(s)}$/SM catalyst had lower acidity than those of the Ni/SM and NiMo$_{(c)}$/SM. These facts can be explain that in sequential impregnation step, the impregnated Mo metal may be dissolved when impregnating with Ni in further step that caused the decrease of the Mo metal. Moreover, Mo metal was also prevented the Ni metal to be impregnated on the SM. It was shown in Table 1 that the Mo metal was predominantly impregnated onto the SM. The specific surface area, average pore diameter, and total pore volumewere shown in Table 2. The surface area decreased after the metal loaded.

**Table 2 Specific surface area, pore diameter and pore volume of Silica**

| Sample | Specific surface area ($m^2/g$) | Pore diameter (n) | Pore volume (cc/g) |
|---|---|---|---|
| Silica (SM) | 550,08 | 7,98 | 1,10 |
| Ni/SM | 457,69 | 8,98 | 1,03 |
| NiMo$_{(c)}$/SM | 419,08 | 9,56 | 1,00 |
| NiMo$_{(s)}$/SM | 503,68 | 8,29 | 1,04 |

Table 2 showed that the metal loaded loaded increased the pore diameter and decreased the specific surface area. These phenomena may be caused by the small portion of pores were covered by the metals

Pore size classification based on IUPAC could be performed by observing pore size distribution. Isotherm patterns of adsorption desorption were supported by data of pore size distribution of each catalyst. In figure 4, all of catalysts still showed mesoporous materials type. Impregnated metal in the SM sample didn't change support material. It can be concluded after the metal loaded, the material still had a mesoporous character. The pore diameter distribution was also still remain constant after the metals loaded. In the graphs, the sizes of pore distributions were quite even. It showed that pores in silica, whether impregnated or not, had good pore uniformity as shown by its hysteresis loop.

### Catalytic activity Test

**Table 3. Distribution of hydrocracking product**

| Catalyst | Product conversion (wt.%) | | |
|---|---|---|---|
| | Liquid | Coke | Gas |
| Thermal | 6,63 | - | 45,32 |
| Silica (SM) | 20,62 | 0,25 | 77,62 |
| Ni/SM | 40,78 | 5,06 | 51,22 |
| $NiMo_{(c)}$/SM | 43,22 | 15,01 | 37,68 |
| $NiMo_{(s)}$/SM | 36,45 | 10,25 | 51,11 |

Table 3 showed product distribution of hydrocracking of waste lubricating oil. The products consisted of liquid, gas, and coke fractions. Thermal cracking produced gas fraction and the lowest portion of the liquid fraction. The available of metal increased the catalysts activity to produce liquid fraction. The co-impregnated metals had highest liquid and diesel fraction with lowest gas fraction. This result was appropriate with character of the $NiMo_{(c)}$/SM which had highest total acidity.

Products distribution in the liquid fraction was shown in Table 4. The highest selectivity towards gasoline fraction was produced by Ni/SM catalyst and highest selectivity towards diesel was achieved by $NiMo_{(c)}$/SM catalyst. This result was influenced by the pore diameter of the catalyst. The Ni/SM catalyst had smaller pore diameter that can produced smaller molecules, such as gasoline, while that of the $NiMo_{(c)}$/SM fit to produced diesel fraction.

**Table 4 Products distribution in the liquid fraction**

| Catalyst | Product distribution (wt.%) | |
|---|---|---|
| | Gasoline | Diesel |
| Thermal | 3,95 | 2,62 |
| Silika (SM) | 19,37 | 1,26 |
| Ni/SM | 24,73 | 16,03 |
| NiMo(s)/SM | 4,90 | 31,51 |
| NiMo(c)/SM | 9,42 | 33,82 |

## Conclusions

The result showed that the gelatin consisted of Amide A, B, I, II dan III. The SM had pore diameter, specific surface area and pore volume of 7.98 nm, 550 $m^2$/g and 1.10 $cm^3$/g, respectively and showed wormhole-like structure with uniform pore diameter. Total acidity of SM, Ni/SM, $NiMo_{(s)}$/SM and $NiMo_{(c)}$/SM samples was 5.1; 7,1; 6.7 and 7.3 mmol/g. The highest liquid product was achieved by $NiMo_{(c)}$/SM catalyst (43.22 wt.%) with the selectivity for gasoline and diesel fractions was 9.42 and 33.82 wt.%.

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